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# Optimizing Process Conditions in Sequential Oxidative/Reductive Bleaching of Wool

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Domestic wool provides about a third of the needs of the American textile industry. American wool is mainly a byproduct of the meat industry and as such it often contains an excessive amount of stained and pigmented fibers. As a result, its perceived quality and price are significantly lower than its imported (mainly Australian) counterpart. The objective of this research is to improve the value of domestic wool and in particular to develop new technology to bleach stained and pigmented fibers.


## ABSTRACT

**The properties of worsted challis fabric were examined after bleaching by conventional alkaline peroxide bleach and by variations of the Agricultural Research Service (ARS) two-step, single-bath sequential oxidative/reductive process. Whiteness and yellowness indices and mechanical properties of fabrics bleached by the conventional process with 22 g/L (20 mL/L) 30% hydrogen peroxide at 50C and 60C were compared with those of fabrics bleached by the ARS process with (a) 16 g/L peroxide; or (b) 8 g/L peroxide in Step 1 followed by the addition of thiourea (70% of the weight of peroxide) in Step 2; or (c) 22 g/L peroxide in Step 1 followed by modifying the baths to reach an effective peroxide level of either 16 g/L or 8 g/L before the addition of thiourea. ARS-bleached fabrics were whiter or equal to the peroxide-bleached fabrics bleached within the same time and temperature limits. ARS-bleached challis retained its original strength but when compared to the peroxide-bleached challis, lost 11% specific stress, with only slight changes in elastic moduli and % strain at peak stress. Evaluation of fabric hand by the Kawabata Evaluation System (KES-F) showed an increase in the hand expression Shinayakasa, indicating greater softness, flexibility and smooth feeling for the ARS-bleached fabrics.**



## KEY TERMS

**Bleaching**
**Fabric Hand**
**Oxidative/Reductive Bleaching**
**Shinayakasa**
**Wool**


The most effective bleaching regimens for stain incorporate both an oxidative and a reductive bleaching step and are referred to as full bleaching. Such full bleaching is normally a two- or three-step process carried out in separate baths. Initial oxidative bleaching normally makes use of hydrogen peroxide. Subsequent reductive bleaching uses such agents as dithionite, sodium formaldehyde sulfoxylate or thiourea dioxide.[1]

In a series of recent reports,[2-6] patents and patent applications,[7-13] the development of new approaches to full bleaching that integrate the processes into single bath procedures are described (Fig. 1 ).

In conventional processes, initial bleaching with hydrogen peroxide is interrupted by quenching. Residual peroxide can simply be destroyed catalytically and a subsequent reductive bleaching carried out by addition of reducing bleach. In the ARS process, residual peroxide is best utilized in a quick chemical reaction that converts the bath into a reductive medium. When thiourea is added under controlled conditions to the peroxide bath, thiourea dioxide is produced. It then hydrolyzes to sulfinate—the reductive bleaching species.[2,4-8,11,13]

Bleaching for black-hair removal typically is done by initial mordanting with ferrous sulfate, then controlled rinsing to eliminate all iron except that which is selectively adsorbed onto the black fibers. Then, hydrogen peroxide is added, black hairs are bleached by a free-radical mechanism induced by adsorbed iron and overall stain is bleached concomitantly.[14] Here again, we have found that residual peroxide may be utilized by conversion of the bleach bath to a reducing medium by controlled addition of thiourea (Fig. 2). This process is effective for bleaching stains that could have been obscured by the pigmentation. It also eliminates traces of any orange-colored ferric species (from the mordanting) by reduction to soluble ferrous ion.[3,4,9-11,13]

A study[6] by $^{13}C$ NMR of the chemistry of the reductive bleaching process shows that thiourea reacts initially with hydrogen peroxide to form thiourea dioxide (Eq. 1):

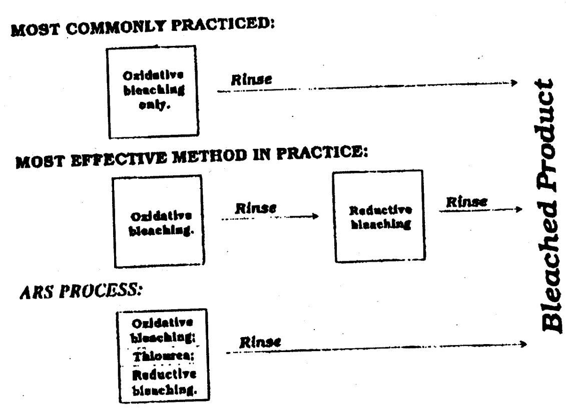


Fig. 1. Bleaching for stain only.

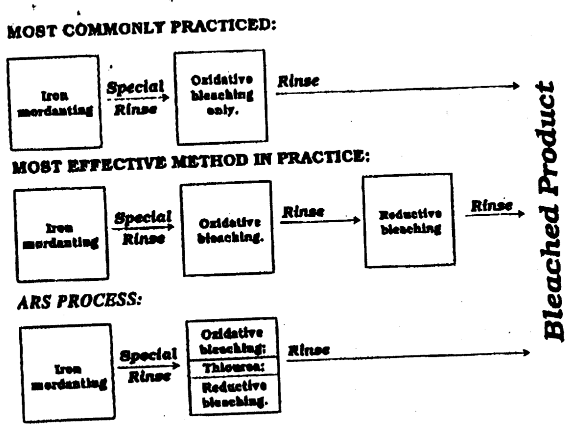


Fig. 2. Bleaching for black hair and stain.

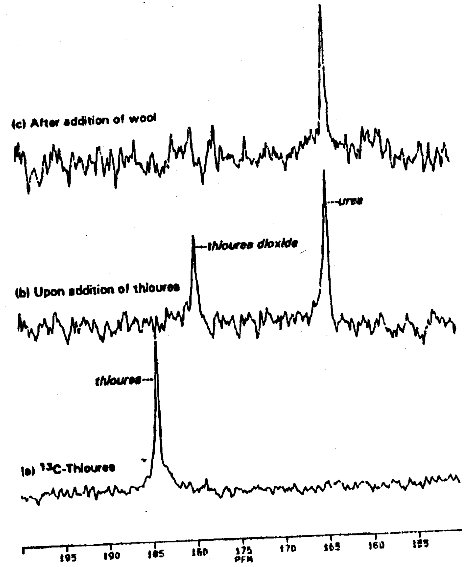


Fig. 3. $^{13}C$ NMR study of ARS bleaching process under mild conditions. $[H_2O_2]$, 8 g/L; T, 50C; final pH, 7.8. (a) Labelled thiourea alone. (b) Peroxide solution (no wool) following addition of thiourea (70% ow 100% $H_2O_2$) at pH 4.5 and subsequent pH adjustment to 7.8; demonstrates incomplete hydrolysis of incipient thiourea dioxide to sulfinate and urea. (c) Complete hydrolysis of thiourea dioxide (noted by absence of its signal) upon addition of wool.

$$\underset{\text{thiourea}}{H_2N\text{-}C(=NH)\text{-}SH} + 2H_2O_2 \xrightarrow{pH<6} \underset{\text{thiourea dioxide}}{H_2N\text{-}C(=NH)\text{-}SO_2H} + 2H_2O \quad \text{Eq. 1}$$

Thiourea dioxide in turn undergoes hydrolysis when the pH of the bath is adjusted to 7-8. It is at this step that the redox potential becomes negative, indicating formation of a reductive medium. NMR shows that thiourea dioxide is hydrolyzed to urea and presumably sulfinate ion, the true reductive species (Eq. 2):

$$\underset{\text{thiourea dioxide}}{H_2N\text{-}C(=NH)\text{-}SO_2H} + 2OH^- \xrightarrow{pH>7} \underset{\text{urea}}{H_2N\text{-}C(=NH)\text{-}OH} + \underset{\text{sulfinate}}{SO_2^{2-}} + H_2O \quad \text{Eq. 2}$$

Sulfinate in turn acts on the wool and is oxidized to sulfate during the bleaching period (Eq. 3):

$$\underset{\text{sulfinate}}{SO_2^{2-}} + 2[O] \longrightarrow \underset{\text{sulfate}}{SO_4^{2-}} \quad \text{Eq. 3}$$

Any residual reductive activity may be quenched at the end of bleaching by addition of a small amount of hydrogen peroxide.

An extension of the single-bath bleaching process was developed to allow subsequent dyeing in the same bath. This is advantageous not only due to the dissipation of all bleaching activity at the end of the ARS process (thus not jeopardizing the dye species), but also because the products of the bleaching step, urea and sulfate ion, are themselves dye assistants.[5]

The procedure for ARS wool bleaching minimizes the amount of thiourea needed without sacrificing resulting whiteness. Thiourea is added in amounts equivalent to 70% of the weight of residual peroxide. $^{13}C$ NMR studies[6] and empirical testing showed that this 3:1 molar ratio of peroxide to thiourea produces a strong reducing medium of high negative potential (-630 mV) and an exclusive urea signal. This indicates the complete conversion of thiourea dioxide to urea and sulfinate.

A typical protocol for ARS full bleaching is outlined below under Experimental.

## Previous Work

Previous work showed how woolen flannel (8.3 oz/yd$^2$) was bleached by the ARS process—a single-bath, two-step, sequential oxidative-reductive system.[3,4] In the individual steps, time, temperature and peroxide concentration were varied. The bath for Step 1 consisted of $H_2O_2$ (22.2 g/L; 30% aqueous), tetrasodium pyrophosphate decahydrate (TSPP, 10 g/L) and Triton X-100 (1.0 g/L) at pH 9.5. In Step 2 the concentration of thiourea varied from 3.07 g/L to 6.66 g/L (46% to 100% o.w. neat peroxide). These prior results showed:

- By varying the thiourea concentration and bleaching times, maximum reduction potential and whiteness could be achieved—after one hour at 60C in Step 1—by the addition of thiourea in Step 2 in amounts at least 70% o.w. neat peroxide with a pH adjustment to 7.4 and 25 minutes of subsequent reductive bleaching.
- By varying the time of oxidative bleaching in Step 1 from 40 to 60 minutes, followed by 25 minutes of reductive bleaching in Step 2 with 6.15 g/L thiourea, (all at 60C) an improved whiteness of 8 WI units could be achieved over the results from 65 to 85 minutes of oxidative bleaching (Step 1) alone.
- Using the same conditions as above, increasing the bath temperature from 60 to 70C increased whiteness by 3 WI (Whiteness Index) units; decreasing the bath temperature from 60 to 55C decreased whiteness by 2 WI units.

In the present work, the use of reduced amounts of peroxide and concomitantly reduced amounts of thiourea for optimum bleaching and minimal fiber damage were investigated. Thiourea concentration was set at 70% o.w. neat peroxide, total bleaching time was a constant 85 minutes and temperature variations were investigated. Thus, the earlier studies were extended to investigate the efficiency of bleaching when the initial peroxide concentration in Step 1 is reduced from 22 g/L to 8 g/L, 16 g/L or 12 g/L. Corresponding modified bleach baths were also investigated where the original 22 g/L peroxide was decreased to 8 g/L or 16 g/L at the end of Step 1 by discarding a portion of the bleach bath. This allowed a lesser amount of thiourea to be needed for running Step 2. These reactions were carried out at 50C and 60C (and 55C in the case of 12 g/L).

Further mechanistic studies also were carried out using $^{13}C$ NMR solution spectroscopy and $^{13}C$-labelled thiourea to follow the conversion of the oxidative bath to the reductive bath.

## Experimental

### Materials

Thiourea[a], thiourea dioxide (formamidinesulfinic acid) and sodium pyrophosphate (TSPP) decahydrate were obtained from Aldrich Chemical Co.[b]

**Table I. Bleaching Conditions, Optimization Runs on Wool Challis**

| Woolen Challis | Step 1 $[H_2O_2]$ (g/L) | Step 1 t (min) | Step 2 $[H_2O_2]$ (g/L) | Step 2 t (min) | T (C) |
|---|---|---|---|---|---|
| 0/0 | 0 | 60 | 0 | 25 | 60 |
| 0/0 (50C) | 0 | 60 | 0 | 25 | 50 |
| 22/22 | 22 | 60 | 22 | 25 | 60 |
| 22/22 (50C | 22 | 60 | 22 | 25 | 50 |
| 16/16T | 16 | 60 | 16 | 25 | 60 |
| 16/16T (50C) | 16 | 60 | 16 | 25 | 50 |
| 8/8T | 8 | 60 | 8 | 25 | 60 |
| 8/8T (50C) | 8 | 60 | 8 | 25 | 50 |
| 12/12T (55C) | 12 | 60 | 12 | 25 | 55 |
| 22/16T | 22 | 60 | 16 | 25 | 60 |
| 22/16T (50C) | 22 | 60 | 16 | 25 | 50 |
| 22/8T | 22 | 60 | 8 | 25 | 60 |
| 22/8T (50C) | 22 | 60 | 8 | 25 | 50 |

Replications: There are three replications. Each replication represents six fabrics (10 grams each) with each treated in its own individual bath, liquor to fabric ratio, 30:1. All results represent mean values of three experiments (18 fabrics).

**Table II. Alkali Solubility of Bleached Worsted Challis**

| Sample | Alkali Solubility (%) |
|---|---|
| 0/0 | 10.3 ± 0.4 |
| 0/0 (50C) | 9.7 ± 0.6 |
| 16/16T | 19.7 ± 1.0 |
| 8/8T | 13.3 ± 0.8 |
| 8/8T (50C) | 17.0 ± 0.5 |
| 12/12T (55C) | 14.6 ± 1.0 |
| 22/8T | 19.9 ± 0.9 |
| 22/16T (50C) | 14.6 ± 0.9 |
| 22/22 | 18.1 ± 1.0 |
| 22/22 (50C) | 18.4 ± 0.5 |

Milwaukee, Wisc. Hydrogen peroxide was a 30% (w/w) aqueous solution obtained from Mallinckrodt Inc., Paris, Ky. Avolan UL-75 amphoteric wetting agent was provided by Mobay Corp., Pittsburgh, Pa. Worsted wool challis, fabric count 48 × 44, fabric weight 3.7 oz/yd$^2$ (warp, 2/50 and weft, 50s), fabric thickness 0.78 mm (at 0.5 gf/cm$^2$) was purchased as 530NC from Testfabrics Inc., Middlesex, N.J. It was received already mildly scoured, rinsed, decatized, but not carbonized.

## ARS Bleaching Technique

Step 1, Oxidative Bleaching: Bleaching was carried out at a liquor to fabric ratio of 30:1, typically using 10 g of woolen fabric and 300 mL of bleaching medium for each of six beakers in an Ahiba Texomat apparatus (Ahiba A.G., Dietlikon, Zurich, Switzerland). Wool was added at ambient temperature to an alkaline bleach bath of the following composition: 30% aqueous hydrogen peroxide (8.0 g/L, equivalent to 2.4 g/L neat hydrogen peroxide), tetrasodium pyrophosphate decahydrate (TSPP; 2.0 g/L), Avolan UL-75 (0.167 g/L). The pH of the bleach bath initially was 9.1. The bath temperature was increased at a rate of 1C/min to 60C (140F) and oxidative bleaching was allowed to proceed for one hour from the addition of wool to the bath. At the end of this stage, the pH of the bleach bath had decreased somewhat (to 8.2-8.7).

Step 2, Reductive Bleaching: The bath, while still at 60C, was acidified to a pH of 5.0-5.5 with acetic acid (56%; approximately 3 mL/L). Then thiourea was added; 1.68 g/L would be equivalent to 70% of the initial hydrogen peroxide, but titration of residual peroxide would probably show about a 10% loss by this time and a concomitant adjustment in the amount of thiourea would be appropriate (though not necessary). Ten minutes was allowed for reaction with residual hydrogen peroxide in the bath (to form thiourea dioxide). Then sufficient aqueous ammonia was added to adjust the pH to 6.8-7.2 to obtain the plummet in potential from +160 mV or higher down to -640 mV to carry out reductive bleaching. Reductive bleaching was allowed to proceed for an additional 25 minutes at 60C.

For bleaching with 12 g/L and 16 g/L peroxide levels, the bath amounts were proportional quantities. For modified ARS bleach baths, Step 1 with 22 g/L peroxide was completed and a proportional volume of the bath was discarded and replaced with water to lower the concentration to 8, 12 or 16 g/L before Step 2.

## Variations in Bleaching for Optimum Conditions

The various conditions for ARS bleaching are shown in Table I. The system of nomenclature, such as 22/8T, indicates in abbreviated form the g/L of 30% aqueous peroxide in the initial step (22), followed by the (sometimes reduced) amount of peroxide in the second step (8) that is converted to a reductive bleach by addition of thiourea (T). The control fabrics [0/0, 0/0 (50C)] were carried through both steps, but without contact with any bleaching medium.

## Fabric Color

Whiteness index (WI; ASTM E-313; 3.387Z - 3Y) and yellowness index (YI; ASTM D-1925; 100 [1.277X - 1.06Z]/Y]) were measured on The Color Machine spectrophotometer (BYK Gardner). Measurements were made using 360° circumferential illumination by a quartz halogen lamp at a color temperature of 2854K (CIE Source C illuminant, CIE Standard 2° observer) at a 45° angle from the sample's normal direction, with sample viewing at 0°.

## Fabric Handle

The Kawabata Evaluation System (KES-F) was used to examine the fabric's physical and mechanical properties, using weight, thickness, tensile, bending, shearing and compression data. For each bleaching condition, the average of three readings was recorded. Instrument settings were as follows:

- Compression: rate of compressing, 0.02 mm/s; maximum force, 50.0 gf/cm$^2$; area compressed, 2.0 cm$^2$/circle.
- Bending: rate of bending, 0.5 cm$^{-1}$/s; maximum curvative, ± 2.5 cm$^{-1}$; sample size, l × w, 15-20 cm × 1 cm.
- Shear: rate of shearing, 0.417 mm/s; maximum shear angle, ±8°; tension on sample, 10 gf/cm. Sample size, l × w, 15-20 cm × 5 cm.
- Tensile: rate of extension, 0.2 mm/sec; maximum tensile force, 500 gf/cm; sample size, l × w, 15-20 cm × 5 cm.
- Fabric Weight (15-20 cm$^2$ area) reported in mg/cm$^2$.

## Alkali Solubility

Alkali solubility of wool after bleaching was determined according to test procedure ASTM D1283-84, Method of Test for Solubility of Wool in Alkali. One gram fabric samples were brought to constant dry weight before and after exposure to 0.1 N sodium hydroxide solution at 65C for one hour. The resulting solutions were then filtered of their fabric residues through sintered glass of medium porosity by vacuum aspiration. Fabric residues were washed, dried and weighed. The degree of damage to wool was then estimated in terms of the loss in fabric

[a] Although thiourea is a cancer-suspect agent, it is easily handled with care and is completely consumed upon reaction with hydrogen peroxide.

[b] Reference to a particular brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

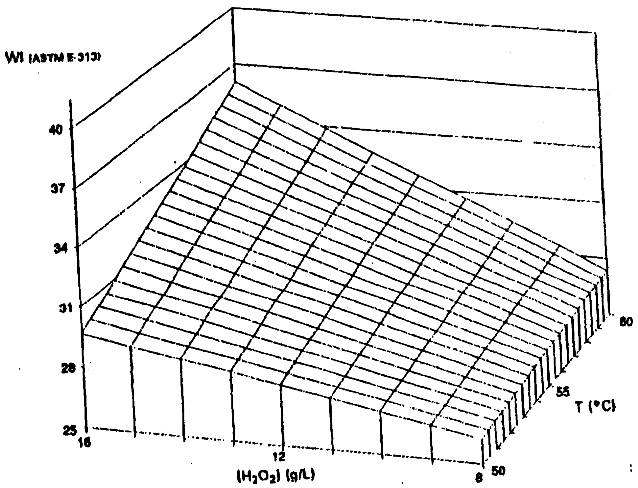


Fig. 4. Effect of temperature and $[H_2O_2]$ on whiteness on bleached worsted challis. Figure constructed from regression equation (Eq. 4) established from five data points (corners and 12 g/L at 55C).

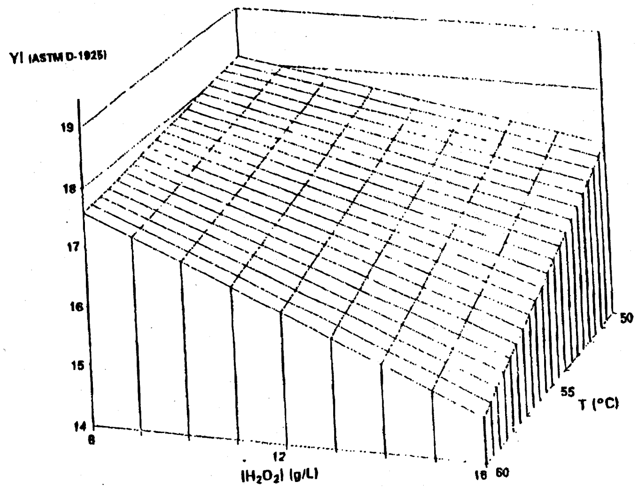


Fig. 5. Effect of temperature and $[H_2O_2]$ on yellowness on bleached worsted challis. Figure constructed from regression equation (Eq. 5) established from five data points (corners and 12 g/L at 55C).

weight as a percentage of the original weight of the sample.

### Testing for Breaking Load and Elongation

Fabrics were measured in the wet state for specific stress, elastic modulus and percentage strain at peak stress on an Instron Model 1122 Analyzer. Analyses were carried out according to ASTM 1682-64, Raveled Strip Method for wet specimens (section 17.2). A load cell, Instron 2511-103, 50-pound load capacity with crosshead speed 200 mm/sec, was used for these fabrics. Force to break was normalized to the fabric linear density (g/cm) with specific stress reported as Newtons cm/gram.

### NMR Spectroscopy

$^{13}$C-NMR spectra were obtained on a Bruker MSL-300 instrument operating at 75.5 MHz. All spectra were obtained with a nine microsec (80C) pulse with a recycle time of 10 seconds. Each spectrum was obtained from 66 8k-data-point scans. Temperature was controlled to within ± 1C. We examined the 8 and 16 g/L (Step 2) reactions at 50C and 60C and at pH ranges of 7.1-7.8 and 8.4-8.9. The procedure involved preparing 15 mL stock solutions of 8.0 g/L ($1.1 \times 10^{-3}$ M) peroxide and 16 g/L ($2.1 \times 10^{-3}$ M) peroxide. The corresponding amounts of thiourea required were $3.3 \times 10^{-4}$ mol and $6.6 \times 10^{-4}$ mol, respectively, wherein the peroxide to thiourea molar ratio was 3.2 in each case. Aliquots (3 mL) were taken for each NMR analysis.

## Results and Discussion

### Reaction Mechanism

The NMR spectrum of $^{13}$C-thiourea (Fig. 3a) was not stable in the presence of hydrogen peroxide at pH 4.5-5.5, but changed instead to the signal for thiourea dioxide (179.8 ppm). When the pH then was raised to >7, complete reaction of the thiourea dioxide was seen, leaving only a signal for the reaction product, urea (164.7 ppm). Under the mildest bleaching conditions (8 g/L, 50C, pH 7.8) however, the thiourea dioxide signal remained pronounced along with the new signal for urea (Fig. 3b). Complete conversion to

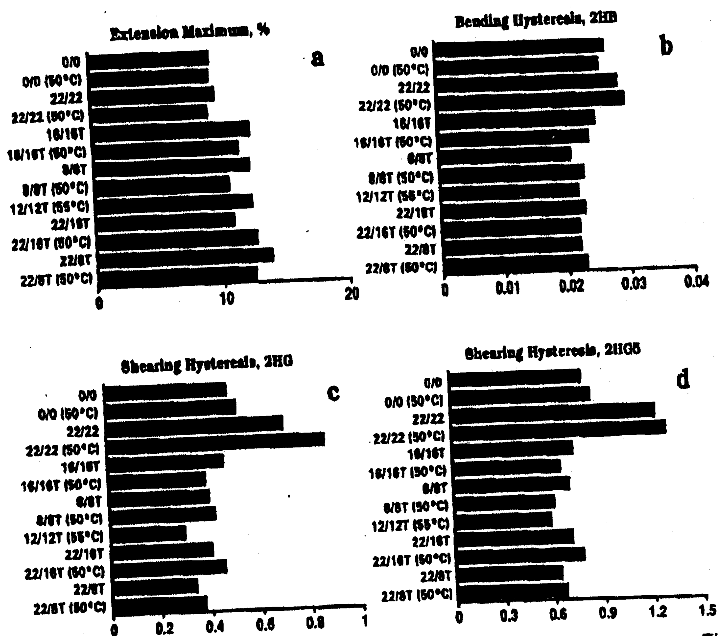


Fig. 6. KES-F characteristic values for bleached worsted challis. Abbreviations: cf. Table I.

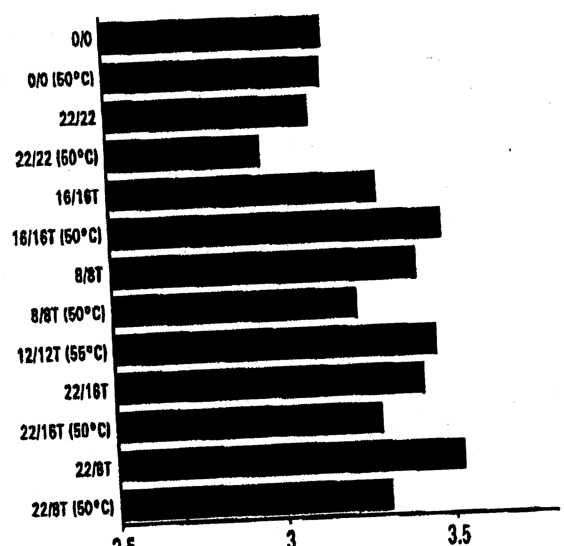


Fig. 7. KES-F Shinayakasa values (x axis) for bleached worsted challis. Abbreviations: cf. Table I.

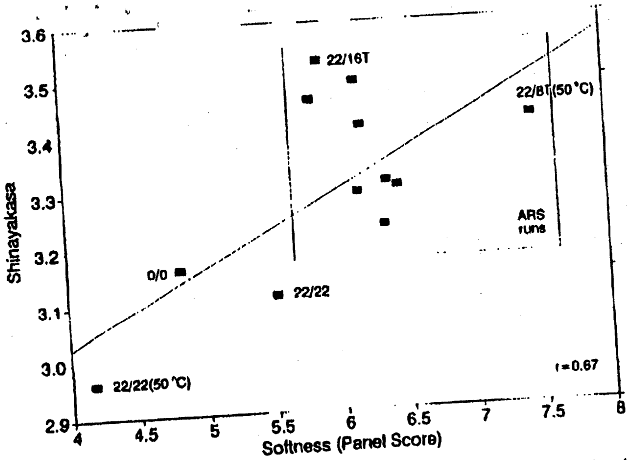


Fig. 8. Shinayakasa vs. subjective score for softness for bleached worsted challis. Abbreviations: cf. Table I. Note cluster of points for ARS-bleached fabrics.

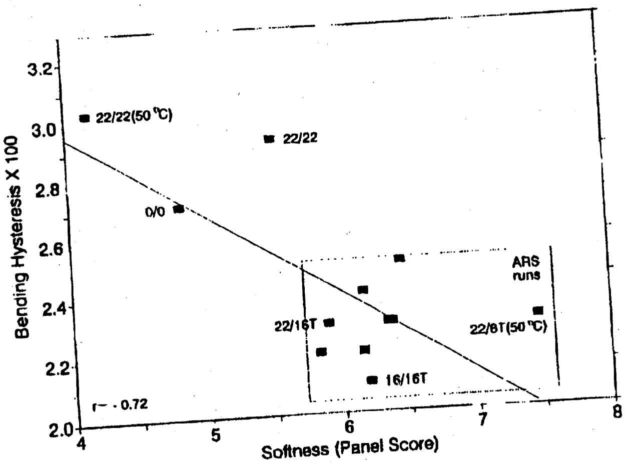


Fig. 9. Bending hysteresis, 2HB, vs. subjective score for softness for bleached worsted challis. Abbreviations: cf. Table I. Note cluster of points for ARS-bleached fabrics.

urea in that case was observed (Fig. 3c) only after wool was added and stirred into the bleaching solution.

These findings support the work of others who found that the decomposition of thiourea dioxide is controlled by the effect of temperature and time, with higher temperature causing greater decrease in thiourea dioxide in the absence of wool. In the presence of wool there was an obvious acceleration of the rate of decomposition of thiourea dioxide.[15]

## Whiteness and Yellowness Indices

The average values for whiteness index (WI) and yellowness index (YI) for 18 replications for each bleaching condition are reported as observed values and were analyzed for statistical differences. The estimated values used to formulate the graphs in Figs. 4 and 5 were derived from data specific to five points (8 g/L at 50C and 60C, 16 g/L at 50C and 60C and 12 g/L at 55C) using the method of least squares from the multiple regression Eqs. 4 and 5 to describe the influence of temperature (T), peroxide concentration $[H_2O_2]$, and the combined effects:

$$WI = 43.745 - 0.42T - 2.89\,[H_2O_2] + 0.066T\,[H_2O_2]\ (R^2 = 0.918) \quad \text{Eq. 4}$$

$$YI = 13.04 + 0.123T + 0.973\,[H_2O_2] - 0.022T\,[H_2O_2]\ (R^2 = 0.900) \quad \text{Eq. 5}$$

Those equations are predictive to estimate the effectiveness of bleaching at specific temperature and peroxide concentration. Overall the process is much more sensitive to temperature at higher peroxide concentrations.

## Fabric Handle

Evaluation of fabric handle by the Kawabata Evaluation System (KES-F) was made on three fabrics selected randomly from the 18 replications per bleaching condition. Each fabric was tested in the warp and weft directions. The most pronounced differences (Fig. 6, a-d) when conventionally-bleached and ARS-bleached fabrics are compared are in the parameters EM% (Extension Maximum at 500 g/cm) in (a), 2HB (Bending Hysteresis) in (b), 2HG (Shearing Hysteresis at 0.5° shear angle) (c) and in 2HG5 (Shearing Hys-

**Table III. Physical/Mechanical Properties Resulting from ARS Bleaching Relative to Conventional Bleaching**

| | Whiteness Index | Specific Stress[a] | Elastic Modulus | % Strain | Kawabata Evaluation System Values: Shinayakasa | Bending Hysteresis (2HB) | Shear Stiffness (G) | Shearing Hysteresis at 0.5° (2HG) | Shearing Extension at 5.0° (2HG5) | Maximum (EM%) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Relative to Conventional Peroxide Bleaching at 60C** | | | | | | | | | | |
| Alkaline peroxide bleaching | | | | | | | | | | |
| 22/22 | 31 | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% |
| For same degree of whiteness as 22/22 | | | | | | | | | | |
| 12/12T (55C) | 31 | 86% | 107% | 96% | 111% | 75% | 80% | 43% | 48% | 128% |
| 22/8T (50C) | 32 | 93% | 100% | 97% | 110% | 78% | 88% | 58% | 58% | 112% |
| For better whiteness than 22/22 | | | | | | | | | | |
| 16/16T | 36 | 89% | 105% | 100% | 110% | 73% | 85% | 57% | 57% | 126% |
| 22/16T (50C) | 36 | 94% | 100% | 96% | 106% | 78% | 86% | 53% | 54% | 129% |
| 22/8T | 37 | 91% | 100% | 97% | 106% | 75% | 87% | 65% | 63% | 130% |
| 22/16T[b] | 41 | 89% | 100% | 97% | 114% | 77% | 83% | 48% | 52% | 142% |
| **Relative to Conventional Peroxide Bleaching at 50C** | | | | | | | | | | |
| Alkaline peroxide bleaching | | | | | | | | | | |
| 22/22 (50C) | 29 | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% | 100% |
| ARS runs | | | | | | | | | | |
| 16/16T (50C) | 29 | 92% | 100% | 97% | 109% | 76% | 85% | 48% | 47% | 116% |
| 22/8T (50C) | 32 | 94% | 100% | 102% | 116% | 76% | 88% | 47% | 55% | 120% |
| 22/16T (50C) | 36 | 96% | 100% | 100% | 112% | 76% | 85% | 43% | 51% | 137% |

[a]Relative to unbleached fabric, no bleached samples showed losses in specific stress. [b]Best protocol for ARS bleaching.

**Table IV. Mechanical Properties**

| | |
|---|---|
| Specific Stress: | Tensile strength |
| Elastic Modulus: | Resistance to extension |
| % Strain at Peak Stress: | Elongation at the breaking point |
| KES Shinayakasa: | Smooth feeling |
| KES Bending Hysteresis (2HB): | Resistance to return to position following bending |
| KES Shear Stiffness (G): | Stiffness to skewing within fabric plane |
| KES Shearing Hysteresis (2HG; 2HG5): | Resistance to return to position following skewing (at 0.5° or 5.0°) |
| KES Maximum Extension (EM%): | Extension under 500g load |

teresis at 5° shear angle) in (d). These parameters, KES characteristic values, are the main contributors to the KES hand expression Shinayakasa, which indicates softness, flexibility and smooth feeling. Shinayakasa is a standard of hand evaluation for women's thin dress fabric,[16] the type of fabric used in this study. Shinayakasa results are shown in Fig. 7. These objectively derived hand-ranking scores were compared to subjective panel scores for softness (Fig. 8) where control, 0/0 (50C), was assigned a score of 5 on a scale of 1-10 (10 being softest). Fig. 9 shows the correlations of bending hysteresis, 2 HB, with the panel scores.

Chemical damage from bleaching is reported (in terms of alkali solubility) in Table II. The alkali solubility of undamaged wool has been reported as 12-13% and for damaged wool, greater than 18%.[17] By 30%, mechanical properties have deteriorated considerably.[18] The values for alkali solubility of ARS- and conventionally-bleached fabrics in Table II are within the range of minimal damage.

## Mechanical Property Testing

Mechanical properties of fabrics bleached by the various bleaching regimens are shown in Table III. These results are grouped according to the degree of whiteness achieved. The specified mechanical properties may be loosely related to the terms listed in Table IV.

Note that the percentages given in Table III are relative to the values obtained from fabrics conventionally bleached (85 minutes oxidative bleaching only; 60 or 50C; [30% aq $H_2O_2$] = 22 g/L). From the loose descriptions in Table IV, the relative KES values under 100% for 2HB, G, 2HG and 2HG5 and over 100% for EM% and Shinayakasa indicate improved softness characteristics. ARS-bleached fabrics exhibit the same or better whiteness as conventionally-bleached fabrics. The added benefit is improvement in the mechanical properties related to softer fabric handle.

## Conclusions

The study done on wool challis fabric has led to the development of a standard bleaching regimen for optimum bleaching by the ARS single-bath process. That regimen (22/16T) calls for bleaching at 60C and allows for the dilution of the peroxide bath after the first step to save on the amount of required thiourea in the second step. Other conditions are also presented for improved bleaching by the ARS process, in which peroxide concentration and temperature differ from 22/16T. The optimum regimen and the other conditions all produced levels of whiteness significantly in excess of alkaline peroxide bleaching over the same time period, peroxide concentration and temperature.

From the mechanical studies on the challis samples it was concluded that strength loss from ARS bleaching is minimal relative to conventional oxidative bleaching (22/22) and that alterations in extensibility, bending and shearing characteristics contribute to an overall increase in softness and smooth handle for these ARS-bleached fabrics.

Despite the two drawbacks—the use of thiourea (though it is completely consumed) and the need for careful pH control—the ARS process gave the highest achievable whiteness, permitted full bleaching in a single bath and imparted increased fabric softness over fabrics conventionally bleached with alkaline hydrogen peroxide.

In the following paper,[19] wool bleaching studies are expanded to examine the ARS process *(1)* on woolen flannel, especially to investigate the effects of photoexposure; and (2) on wool/cotton blended fabric and all-cotton fabric, to broaden the applicability of the ARS process to cellulosic fibers.



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